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SELECTIVE TRANSFORMATION OF CARBONYL LIGANDS TO ORGANIC MOLECULES

Progress Report

for Period 9/1/89 - 11/14/92

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PRINCIPAL INVESTIGATOR

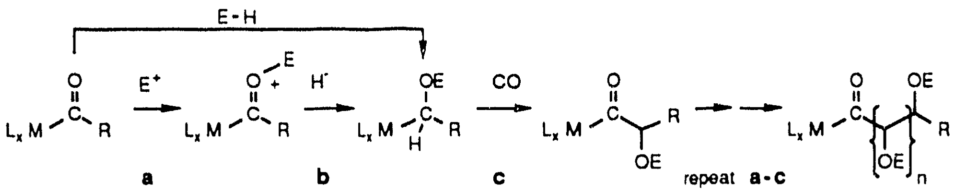
Abstract

Studies on the carbonylation of (η^5-indenyl)(L)(CO)Ru-R complexes (L = CO, PPh_3; R = CH_2OMe, CH_3) have been completed. Particularly noteworthy is that the methoxymethyl complexes readily transform to their acyl derivatives under mild conditions that leave their iron congeners inert towards CO. Surprisingly, even (η^5-indenyl)$(PPh_3)_2$Ru-CH_3 carbonylates and gives (η^5-indenyl)(PPh_3)(CO)Ru-C(O)CH_3. Attempts to carbonylate α-alkoxyethyl analogs (η^5-indenyl)(L)(CO)Ru-CH(OR)CH_3 [L = PPh_3, PEt_3, $P(OMe)_3$] afford (η^5-indenyl)(L) (CO)Ru-C(O)CH_2CH_2OR, which are isomeric to the expected α-alkoxypropionyl complexes [Ru]-C(O)CH(OR)CH_3. Attempts to use this rearrangement for incorporating additional CO into the ligand chain are in progress. Mechanistic studies on the "non catalyzed" hydrosilation of the manganese acyls $(CO)_5$Mn-C(O)CH_2R (R = H, OCH_3, CH_3) with Et_3SiH and of cobalt acetyls $(CO)_3(PR_3)CoC(O)CH_3$ with several monohydrosilanes have been completed. The cobalt acetyls cleanly give ethoxysilanes (not acetaldehyde), and the manganese acyls provide α-siloxyvinyl complexes *Z*-$(CO)_5$Mn-C($OSiEt_3$)=CHR (R = H, CH_3, OCH_3). Carbonylation and protolytic cleavage of the latter generate pyruvoyl complexes $(CO)_5$Mn-COCOR (R = CH_3, CH_2CH_3), formally the products of net "double carbonylation" sequences. Studies in progress are concerned with how manganese complexes as diverse as $(CO)_5$Mn-Y [Y = C(O)R, R, Br - but not $SiMe_3$ or $Mn(CO)_5$] and (η^3-C_3H_5)$Mn(CO)_2$L [but not $CpMn(CO)_3$ or $CpMn(CO)_2$ (η^2-$HSiR_3$)] function as efficient hydrosilation catalysts towards $Cp(CO)_2FeC(O)CH_3$, for example. These reactions cleanly afford fully characterized α-siloxyethyl complexes Fp-CH($OSiR_3$)CH_3 under conditions where typical Rh(I) hydrosilation catalysts are inactive. Several of these manganese complexes also catalytically hydrosilate organic esters, including lactones, to their ethers R-CH_2OR'; these novel ester reductions occur quantitatively at room temperature and appear to be general in scope. Efforts to develop a phosphide-phosphine "switch" for controlling the reactivity (and stereochemistry) of acyl ligand reduction on Cp(PPh_2H)(CO)FeC(O)CH_3 / Cp(PPh_2)(CO)FeC(O)CH_3^{-1} have been completed. These studies involved attempts to generate (and reduce) siloxycarbene complexes Cp(PPh_2)(CO)Fe=C($OSiR_3$)CH_3 and Cp(PPh_2R)(CO)Fe=C($OSiR_3$)CH_3^+.

Selective Transformation of Carbonyl Ligands to Organic Molecules

I. Overview and Objectives: Poly(alkoxymethylene)acyl complexes from Carbon Monoxide

We are developing "novel" organometallic systems and coordinated ligand reactions for converting carbon monoxide into poly(alkoxymethylene)acyl ligands (eq. 1). These poly(alkoxymethylene)acyl complexes result from coupling acyl ligand reduction (**a/b**) with subsequent carbonylation steps (**c**). Two approaches to acyl ligand reduction involve (1) separate electrophilic activation of an acyl ligand (**a**) followed by hydride transfer to its oxycarbenoid derivative (**b**) and (2) one-step addition of E-H (R_3Si-H) across the acyl ligand.[1]



(1)

Selecting the organometallic system ML_x for sequentially iterating these ligand reactions, however, poses a challenge due to their antithetical requirements. The CO-insertion step **c** requires a labile metal center, particularly since carbonylation of an α-alkoxyalkyl complexes is notoriously difficult. Steps **a** and **b** are limited to a robust (nonlabile) metal center on ML_x in order to restrict the reduction chemistry to the acyl ligand. Otherwise, reduction at the metal center would remove the ligand.

This project involves two overlapping objectives. (1) Appropriate organometallic systems ML_x for coupling the incongruous ligand skeletal reactions **a/b** and **c** must be developed. (2) The stereochemistry of each emerging chiral center (step **b**) must be controlled. Satisfying these objectives places severe constraints on designing our "active site" on ML_x, but also addresses structure-reactivity issues of fundamental importance to homogenous catalysis. These are discussed in the remainder of the progress report and accompanying proposal documents. But first, several highlights of the current grant period are noted:

1. We now have two procedures that use the "indenyl effect" to drive otherwise infeasible carbonylation reactions. In particular, indenyl ruthenium alkyl complexes R-Ru(L)(CO)(η^5-C_9H_7) exhibit incredibly facile carbonylation reactivity: *We now can carbonylate the α-alkoxyakyl complexes under conditions that their η^5-Cp congeners are inert.*

2. We have discovered a new kind of hydrosilation catalysis involving organometallic acyl complexes (**a/b** in eq. 1, E-H = H-SiR_3). Manganese complexes $YMn(CO)_5$ (Y = Br, CH_3, C(O)CH_3, C(O)Ph, etc.) function as far more effective hydrosilation catalysts towards iron acyl compounds RC(O)Fe$(CO)_2$Cp, for example, than do standard Rh(I) hydrosilation catalysts. More importantly, we believe that this manganese hydrosilation catalysis involves a conceptually novel odd-electron mechanism.

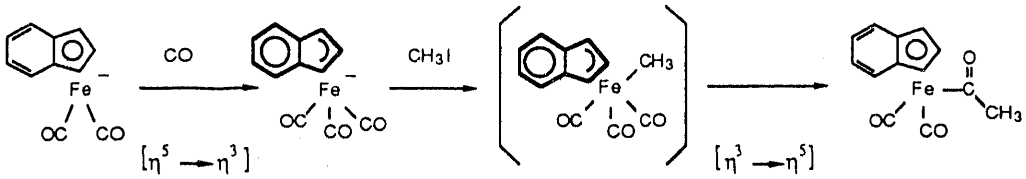
3. This manganese hydrosilation catalysis also reduces organic esters under extremely mild conditions. We anticipate that a number of other useful applications to organic synthesis soon will be found.

4. Catalytic hydrosilation of the iron and ruthenium acetyl complexes CH_3C(O)Fe(CO)(L)Cp (L = PR_3, P$(OR)_3$) fulfills two objectives. First, extremely high diastereofacial selective hydrosilation is observed. Depending on the choice of manganese $YMn(CO)_5$ or Rh(I) precatalyst, either RR(SS) or RS(SR) diastereomers are favored. Second, altering the catalysis conditions selectively transforms the α-siloxyethyl complexes to vinyl derivatives CH_2=CH-Fe(CO)(L)Cp, literally as one-pot operations.

5. We have found a new approach to "double carbonylation" of labile manganese acyl complexes $RCH_2C(O)$-$Mn(CO)_5$. Treating with $HSiEt_3$ produces α-siloxyvinyl derivatives $RCH{=}C(OSiEt_3)$-$Mn(CO)_5$, which convert to the α-ketoacyl complexes $RC(O)C(O)$-$Mn(CO)_5$ after carbonylation and protonolysis. Most other mono- and dihydrosilanes add across the acyl ligand of $RCH_2C(O)Mn(CO)_5$ and generate their α-siloxyethyl compounds, $CH_3CH(OSiR_3)Mn(CO)_5$.

II. Carbonylation of α-Alkoxyalkyl Complexes

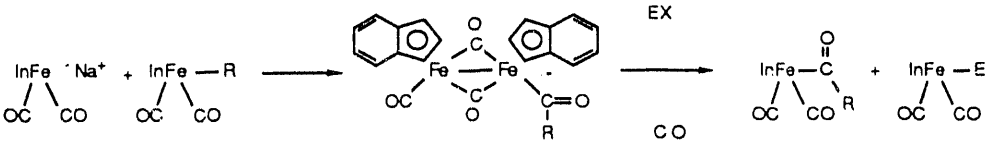
We previously established that substituting the η^5-indenyl ligand (In) for the Cp group promotes the carbonylation of alkyl complexes, particularly H_3C-$Fe(CO)(L)(In)$ complexes.[2] This enhanced carbonylation reactivity originates from reversible η^5/η^3 indenyl ring slippage[3] that successively couples CO association at the metal with alkyl-CO migration. Indirect evidence is available that links reversible η^5/η^3 indenyl ring shifts with facile carbonylation. Nucleophilic $InFe(CO)_2^-Na^+$ thus irreversibly incorporates CO (at 1 atm) and generates $(\eta^3\text{-In})Fe(CO)_3^-$ Na^+, for which an X-ray structure determination established its nonplanar η^3-indenyl ligand.[4] Alkylation of this metalate and then alkyl migration accounts for the observed acetyl product.



This enhanced reactivity does not extend to the more relevant (eq. 1) methoxymethyl compounds. For example, $MeOCH_2Fe(CO)(PPh_3)In$ when treated with 80 atm of CO only replaces ligated phosphine by CO.[2] Attempts to further promote this carbonylation by hydrogen bonding, organometallic Lewis acids,[5] or even electron-transfer catalysis[6] were unsuccessful. We now have devised the following two procedures using η^5-indenyl Fe and Ru chemistry that carbonylate α-alkoxyalkyl complexes.

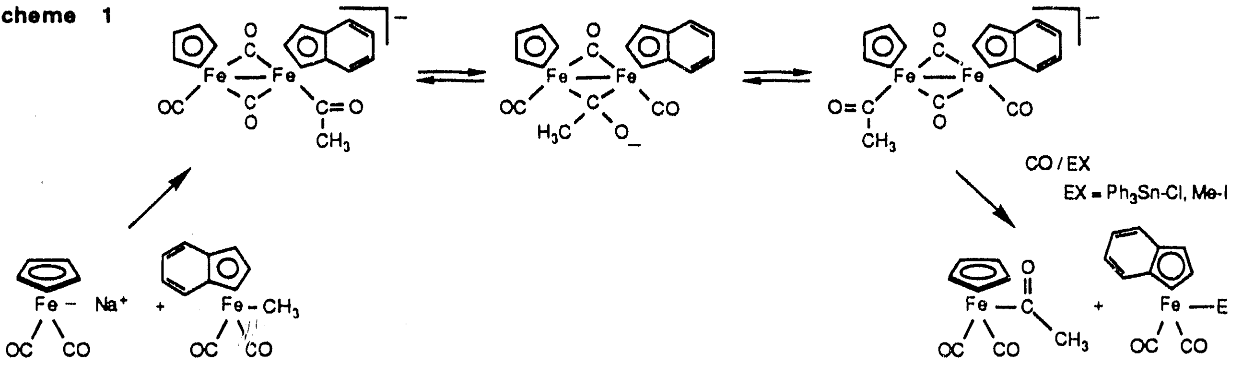
A. Bimetallic Carbonylation using η^5-Indenyl Iron Complexes

Reversible η^5/η^3 indenyl ring slippage is the driving force in a novel two-step, metalate-promoted carbonylation procedure involving $(alkyl)Fe(CO)_2In$ complexes. Treating $CH_3Fe(CO)_2In$ with $InFe(CO)_2^-Na^+$ immediately affords a stable bimetallic acyl compound; intercepting it with an electrophile E-X (MeI or Ph_3SnCl) in the presence of CO (1 atm) produces the acetyl complex $CH_3C(O)Fe(CO)_2In$ (85%).[7]



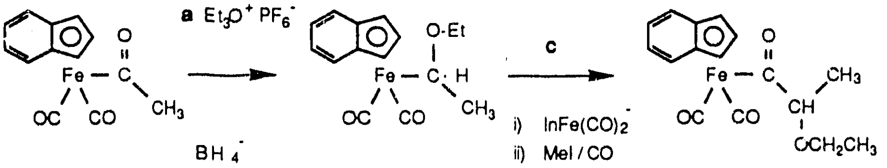
Mechanistic studies of this carbonylation were aided by switching to Fp^-Li^+, Na^+, K^+, and PPN^+ as the metalate; several observations are worth noting. (1) Treating the mixed CpIn bimetallic acetyl with EX regioselectively produces $FpC(O)CH_3$. (2) An X-ray structure determination of this mixed CpIn dimer established that it crystallizes with the terminal acetyl ligand on the CpFe end. (3) In solution, it exists as a 1:1 mixture of the two bimetallic acetyl regioisomers depicted; acetyl group migration between the two Fe centers was studied by ^1H NMR magnetization transfer ($k_1 = 0.33$ sec^{-1} at 22 °C). (4) The μ-oxyalkylidene intermediate in this acetyl shift can be detected and under the appropriate reaction conditions and can

Scheme 1



beconverted to μ-vinylidene compounds, $InCp(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)$.[8]

The significant outcome of these studies is that we successfully carbonylated iron α-alkoxyalkyl complexes with *1 atm. of CO*. Treatment of the methoxymethyl complex $MeOCH_2Fe(CO)_2In$ with $InFe(CO)_2^-$, followed by methyl iodide and CO, affords methoxyacetyl compounds in 60% yields. We used this two-step carbonylation procedure as a one-pot operation in (a) activating, (b) reducing, and (c) carbonylating an acetyl ligand to give its α-ethoxypropionyl iron complex in 47% overall yield (eq. 2).[9]



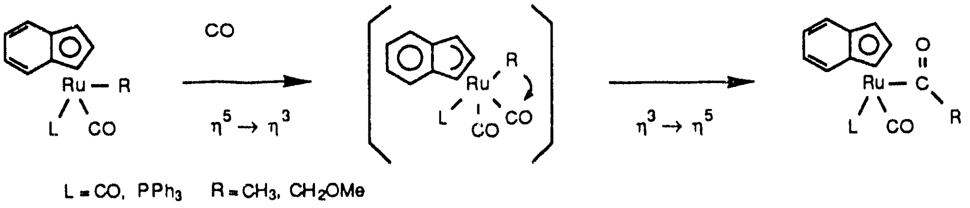
(2)

Our proposed mechanism for this carbonylation requires the presence of at least one indenyl ligand – with its accessible η^5/η^3 ring slippage[10] – on our bimetallic acetyl compounds, both in forming and cleaving them with EX / CO. Overall, this two-step carbonylation procedure involving (i) metalate-promoted alkyl migration, (ii) cleavage of a bimetallic intermediate that gives the mononuclear acyl product, and (iii) indenyl ring slippage represents a conceptually new carbonylation procedure.

B. Indenyl Ruthenium Carbonylation Chemistry

η^5-Indenyl ruthenium alkyl complexes carbonylate under unusually mild conditions (eq. 3).[11] The methyl-to-acetyl carbonylations occurs under 15-85 psig CO in CH_2Cl_2 (22 °C), whereas carbonylation reactions involving CpRu congeners require considerably more vigorous conditions, e.g., 100 atm CO for $Cp(CO)_2RuCH_3$ in nitromethane.[2] A qualitative ranking of the facility for this methyl-to-acetyl carbonylation follows:

$In(PPh_3)(CO)Ru >> \mathbf{In(CO)_2Ru} > In(PPh_3)(CO)Fe >> In(CO)_2Fe >$
$Cp(PPh_3)(CO)Fe > Cp[P(OMe)_3](CO)Fe > Cp(CO)_2Fe > Cp^*(CO)_2Fe >> \mathbf{Cp(CO)_2Ru}$

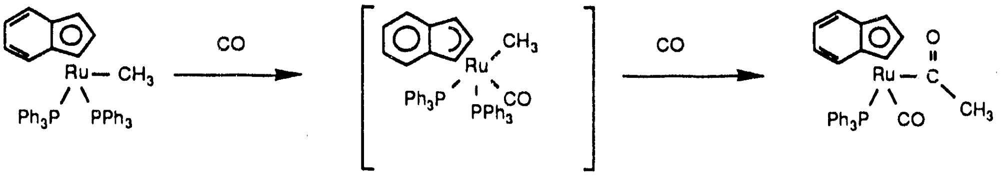


(3)

The major breakthrough is that we now can directly carbonylate alkoxymethyl complexes! For example, $MeOCH_2Ru(PPh_3)(CO)(\eta^5\text{-}C_9H_7)$ quantitatively transforms (12 h) to its acyl derivative $MeOCH_2C(O)Ru(PPh_3)(CO)(\eta^5\text{-}$

C_9H_7) in CH_2Cl_2 with 85 psig CO.[12] It is worth noting that considerable effort was required to synthesize and characterize the eight methyl / acetyl and methoxymethyl / methoxyacetyl complexes depicted. Many standard synthetic procedures for "Fp" chemistry, especially those requiring photolysis, cannot be applied to indenyl ruthenium systems.

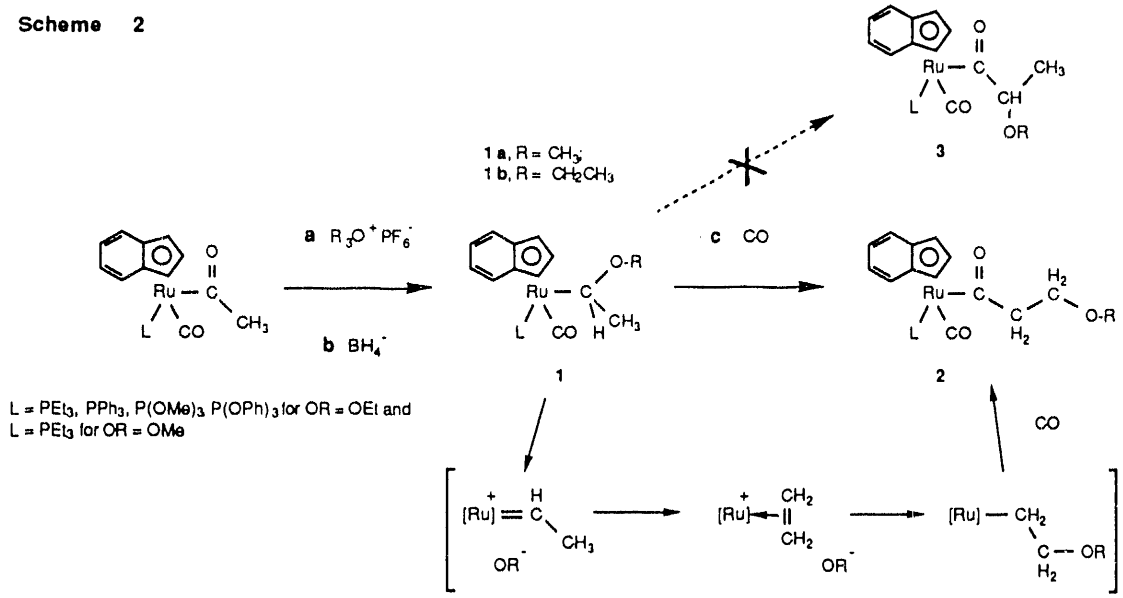
Further support for InRu alkyl complexes associating CO (commensurate with η^5/η^3-indenyl ring slippage) during their carbonylation reactions derives from the results of carbonylating In(PPh3)2Ru-CH3 (eq. 4). This complex efficiently incorporates CO (≤ 50 psig, 22 °C in CH_2Cl_2) to give an acetyl complex in which a phosphine ligand also has been replaced by CO. Note that the Cp analog, Cp(PPh3)2Ru-CH3, does not incorporate CO (80 psig).[11]



(4)

Our working hypothesis for the increased carbonylation reactivity of InRu alkyl complexes over their iron counterparts engenders η^5/η^3 indenyl ring slippage (with rapid association of CO) to generate putative η^3-indenyl intermediates (η^3-In)(L)(CO)2Ru-R (eq. 3). Subsequent η^3 to η^5 indenyl ring slippage on these intermediates then couples with either CO dissociation or alkyl-CO migratory insertion. For the iron congener, CO dissociation kinetically predominates, and regenerates the alkyl. The enhanced Ru-CO bond energies (vs Fe-CO) favor alkyl-CO migration, presumably due to less bond breaking in its transition state. If this hypothesis is correct (labeling and kinetic studies are contemplated), then the thermodynamically more stable (η^3-indenyl)ruthenium intermediate (with respect to CO dissociation) may be more reactive due to the η^3 to η^5 indenyl shift driving the alkyl-CO migration step.

Scheme 2

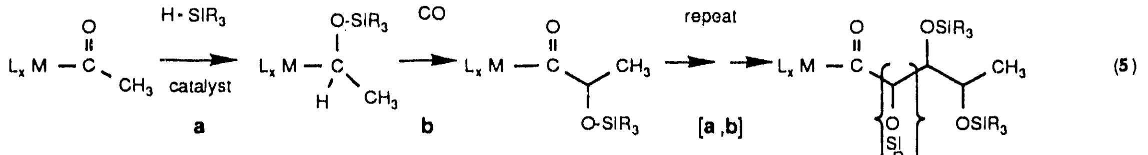


Synthetic studies on carbonylating α-alkoxyethyl complexes **1** (Scheme 2) have just been completed.[12] Surprisingly, treatment of **1** with 80 psig CO in CH_2Cl_2 or benzene cleanly affords β-alkoxypropionyl complexes **2**, with no evidence of the α-alkoxypropionyl isomers **3**. (Congeneric iron α-alkoxypropionyl had been previously prepared,[9] eq. 2). Five examples of **2**, L = PEt3, PPh3, P(OMe)3, P(OPh)3 for OR = OEt and L = PEt3 for OR = OMe have been fully characterized.

A plausible reaction pathway for this carbonylation also appears in Scheme 2. In this working hypothesis, rear rangement of the α-alkoxyethyl **1** to its isomeric β-alkoxyethyl complex **2** follows after ionizing alkoxide, presumably as a tight ion pair. Subsequent ethylidene to ethylene rearrangement via hydride transfer[13] and nucleophilic addition of alkoxide to η^2-ethylene compounds[14] are well known. Although rare, the overall α- to β-alkoxyethyl ligand rearrangement is precedented,[15] and in our examples, alkyl-CO migratory insertion of the latter should be kinetically favored. Alternative mechanisms for transforming **1** to **2**, such as those involving alkoxide or α-hydride migration to the metal (perhaps commensurate with reversible η^5/η^3 indenyl ring slippage) also will be tested. This unexpected carbonylation sequence poses both a (temporary) setback as well as new opportunities for synthesizing poly(alkoxymethylene)acyl complexes, vide infra.

III. Hydrosilation of Organotransition Metal Acyl Complexes

Our original objective entailed developing catalytic hydrosilation for transforming organometallic acyl complexes to isolable α-siloxyalkyl derivatives and then to poly(siloxymethylene)acyl compounds (eq. 5). This objective temporarily has been sidetracked in order to explore hydrosilane reactions with organometallic alkyl and acyl complexes. First, our choice of acyl substrates and reaction conditions for generating α-siloxyethyl compounds will be presented.



(5)

Table 1 summarizes the selection of acetyl complexes that we use in ongoing hydrosilation studies.[16] Iron and ruthenium acyls, entries 1-3, require catalysts in order to give α-siloxyalkyl derivatives,[17,18] whereas manganese acetyls, entry 4, do not.[19] Rhodium catalysts are *not* required for hydrosilating these manganese and cobalt (entry 5) systems.[20] An important development was that the same manganese acetyl (and benzoyl) compounds are extremely efficient hydrosilation catalysts towards iron and ruthenium acyls: the manganese acyl remains intact until the iron or ruthenium acyl substrate is consumed.[21] More recent studies have established that a variety of manganese complexes $YMn(CO)_5$ also function as excellent hydrosilation catalysts towards organometallic and organic acyl substrates.[21]

We prefer using Fp acyl compounds (entry 1) in exploratory studies for developing new catalysts: The resulting α-siloxyalkyl derivatives $FpCH(OSiR_3)R$ are both stable and easily isolated or quantified spectroscopically. $FpC(O)CH_3$ is particularly convenient for mechanistic studies and FpC(O)Ph is our choice for a "difficult" substrate.[17] Chiral iron acetyl substrates, entry 2, are being used in assessing diastereofacial selectivity in forming the new stereogenic center during hydrosilation. Iron and ruthenium indenyl analogs should allow coupling this diastereoselective hydrosilation reaction **a** with a subsequent carbonylation step **b**.

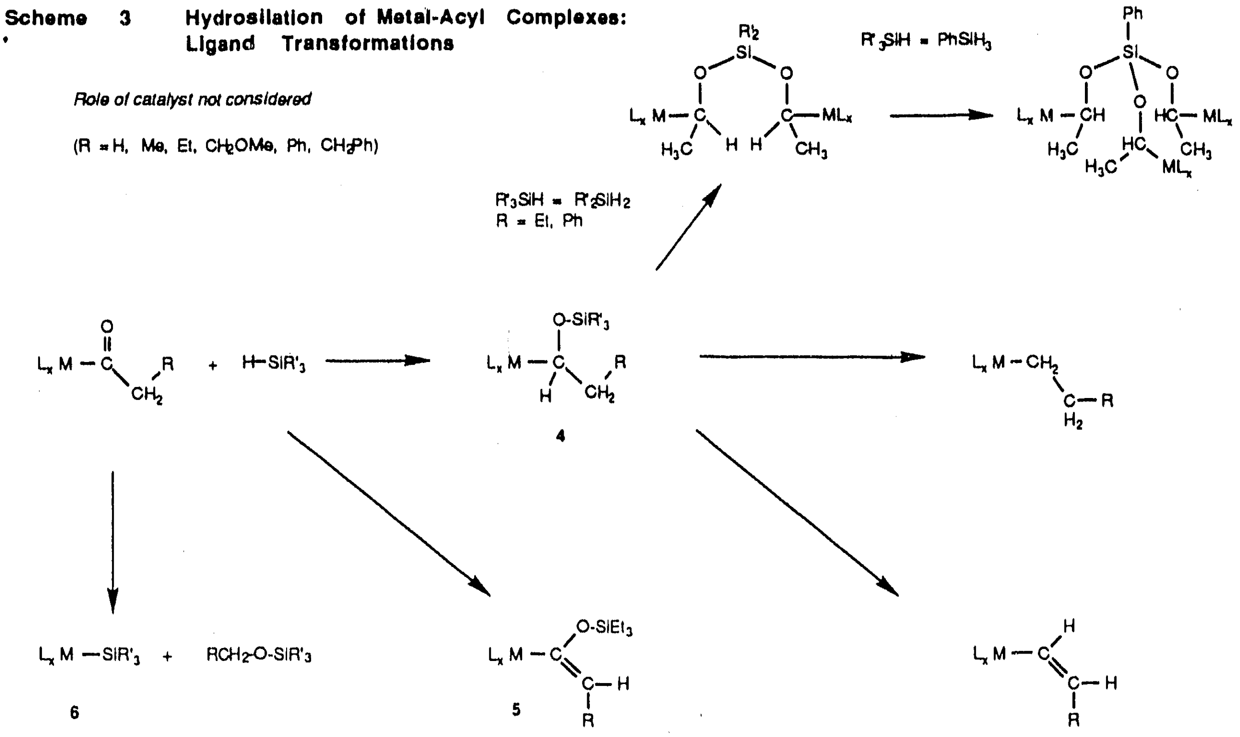
An important albeit unexpected development is that hydrosilation of acyl compounds, with or without an added catalyst, also affords a variety of ligand transformations and products noted in Scheme 3. With judicious choice of catalyst, silane, and reaction conditions, the α-siloxyethyl compounds **4** *selectively* undergo further ligand reactions to give bimetallic bridging siloxyethyl derivatives, vinyl compounds, or the fully reduced ethyl complexes.[16] Alternative and sometimes competing pathways that we also have observed afford α-siloxyvinyl complexes **5** or even metal silyls **6** via hydrosilation at the metal center that eliminates a silyl ether RCH_2OSiR_3. These ligand reactions will be briefly described in the following sections.

When our studies were initiated the prevailing belief was that labile metal acyl compounds would add $HSiR_3$ and

Scheme 3 Hydrosilation of Metal-Acyl Complexes: Ligand Transformations

Role of catalyst not considered

(R = H, Me, Et, CH_2OMe, Ph, CH_2Ph)



eliminate aldehyde,[22] a reaction that we have never observed, vide infra. α-Siloxyalkyl compounds had only been invoked as initial products of metal silyl compounds interacting with aldehydes.[23,24] In the interim, Moro-oka and co-workers also have published on the reactions of acetyl complexes with hydrosilanes. Surprisingly little overlap exists between the results of the Japanese workers and us, since they emphasized either Rh(I) catalysis (even when unwarranted[18]) or hydrosilane reactions under thermal conditions that removed the organic ligand.[25] We also note that Hossain recently has reported synthesizing several α-siloxyalkyl Fp complexes by treating Fp^- Na^+ sequentially with an aldehyde and then with trimethylsilyl triflate.[26]

Table 1 Hydrosilation of Metal Acyl Complexes

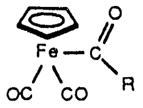
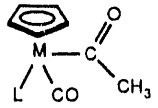
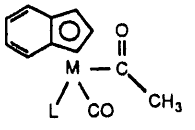
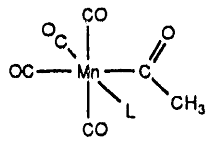
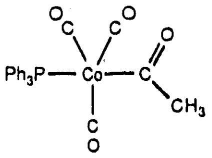
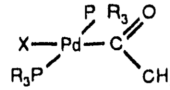
Entry	Substrate	Catalyst	Silane
1.		A. $(PPh_3)_3RhCl$ and other Rh(I)	R_2SiH_2 $PhSiH_3$
		B. $L(CO)_4Mn$-Y, Y = Br, R, C(O)R	R_3SiH, R_2SiH_2, $PhSiH_3$
		C. $Co_2(CO)_8$ and other Co(I)	R_3SiH, R_2SiH_2, $PhSiH_3$
2.	 M = Fe, Ru L = PR_3 $P(OR)_3$, t-BuNC	A. $(PPh_3)_3RhCl$ and other Rh(I)	R_2SiH_2
		B. $L(CO)_4Mn$-Y, Y = Br, R, C(O)R	R_2SiH_2
3.		A. $(PPh_3)_3RhCl$ and other Rh(I)	R_2SiH_2
		B. $L(CO)_4Mn$-Y, Y = Br, R, C(O)R	R_2SiH_2

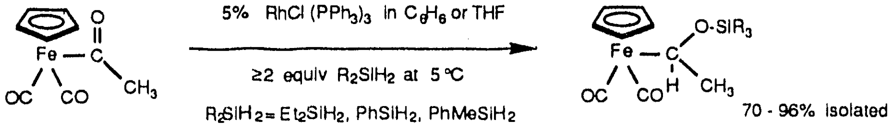
Table 1, Continued

4.	 L = CO, PR$_3$	A. None added B. $(PPh_3)_3RhCl$	R_3SiH, R_2SiH_2, $PhSiH_3$ R_2SiH_2
5.		A. None added B. $(PPh_3)_3RhCl$	R_3SiH, R_2SiH_2 R_2SiH_2
6.		*Proposed:*	

A. Homogeneous Catalytic Hydrosilation of Organometallic Acyl Complexes

1. Rhodium-Catalyzed Hydrosilation of Iron and Ruthenium Acetyl Complexes $CH_3C(O)M(L)(CO)Cp$ (L = CO, PR_3, $P(OR)_3$): Stereochemistry

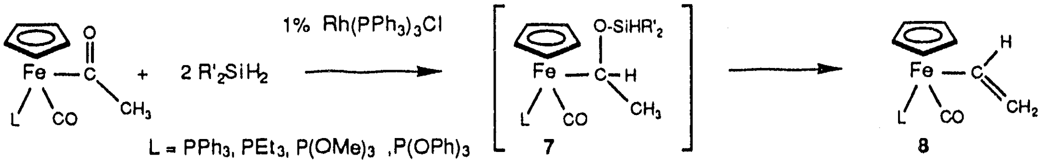
We demonstrated the $Rh(PPh_3)_3Cl$-catalyzed hydrosilation of Fp acetyl and related acyl complexes with dihydrosilanes. A number of these stable Fe and Ru $M(CO)_2Cp$ α-siloxyalkyl products (Cp = η^5-C_5H_5, η^5-C_5Me_5, η^5-indenyl) have been fully characterized (eq. 6).[16,17]



(6)

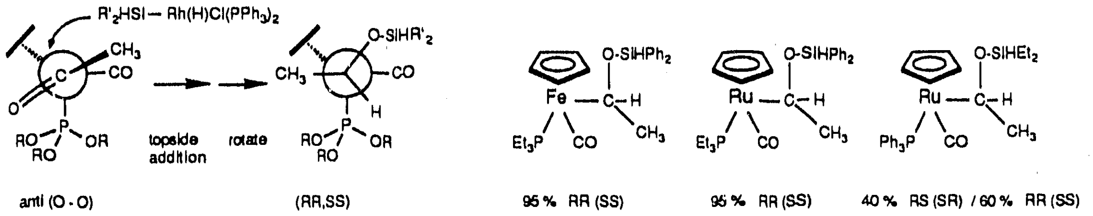
Rhodium-catalyzed hydrosilation of iron acyl compounds suffers from two draw-backs. First, this reaction is of limited scope. Monohydrosilanes don't work, and many Fp(acyls) react sluggishly with dihydrosilanes. Second, Rh-catalyzed dehydrogenative coupling of dihydrosilanes efficiently competes with acyl hydrosilation. This imposes the need for excess silane and also engenders messy workup procedures. Other rhodium systems tried to date are less effective than $Rh(PPh_3)_3Cl$.

Phosphine- and phosphite- substituted iron acetyl compounds are extremely reactive substrates even when using 1% $Rh(PPh_3)_3Cl$ and either Et_2SiH_2 or Ph_2SiH_2, except that vinyl complexes $Cp(L)(CO)FeCH{=}CH_2$ (**8**) are the final products (eq. 7). These vinyl compounds have been isolated and fully characterized.[27]



(7)

Substantial concentrations of the α-siloxyethyl intermediates **7** accumulate in dilute C_6D_6 solutions, which we examined by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Analogous CpRu (L = PPh_3, PEt_3), and (η^5-indenyl)Ru (L = PPh_3) acetyl compounds also undergo similar Rh(I)/dihydrosilane catalysis, with the ruthenium congeners affording isolable products.[28] These reactions are diastereoselective under certain conditions, and favor the RR(SS) diastereomer (eq. 8). Typical results appear below for CpFe and Ru phosphine acetyl systems; several examples have been isolated analytically pure.



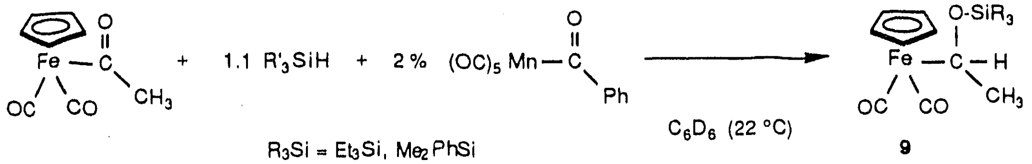
(8)

We assigned the structure of the predominant RR(SS) α-siloxyethyl diastereomer by NMR spectroscopy.[29] Interestingly, this stereoselectivity is opposite to that observed during hydride transfer to the alkoxycarbene compounds, $Cp[P(OR)_3](CO)Fe{=}C(OCH_3)CH_3^+$.[30] The complementary diastereofacial selectivity observed during both acyl ligand reduction procedures apparently originates with the phosphite group sterically blocking reagent access to opposite faces of the acyl and the alkoxycarbene ligands.

In recent studies, we have isolated and fully characterized two iron α-siloxyethyl complexes (L = PPh_3, $P(OMe)_3$) after hydrosilation catalysis using $PhC(O)Mn(CO)_5$, albeit as 3.5-5 : 1 mixtures of RS(SR) : RR(SS). Treatment with methanol followed by low-temperature chromatography afforded $Cp(L)(CO)FeCH(OMe)CH_3$, but as 8.5 : 1 RR(SS) : RS(SR) mixtures. Studies are in progress to optimize and understand the diastereoselectivity of rhodium- and manganese-catalyzed hydrosilation of $CH_3C(O)Fe(CO)(L)Cp$ (L = PPh_3, PEt_3, $P(OMe)_3$, $P(OPh)_3$).

2. Manganese Catalysts $YMn(CO)_5$: $Cp(CO)_2Fe\text{-}COCH_3$ as the Test Substrate

An exciting development in our catalysis program is the discovery that $YMn(CO)_5$ complexes function as hydrosilation catalysts. These catalytic systems are far more active and selective than are the rhodium catalysts that we examined. For example, we reported that $PhC(O)Mn(CO)_5$ catalytically adds *monohydrosilanes* to $FpCOCH_3$ (and other acyl complexes); analytically pure trialkylsiloxyethyl compounds are isolated in 80-90% yields after chromatography (eq. 9).[21]



R3Si = Et3Si, Me2PhSi

9

(9)

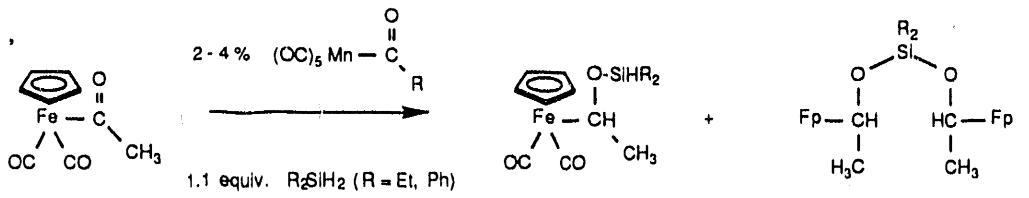
We have since established that choice of manganese catalyst *and* silane controls the hydrosilation reactivity of $FpCOCH_3$ and FpCOPh. A portion of this data appears below for the qualitative ranking of hydrosilation reactivity of 1.5% Mn precatalyst towards $FpCOCH_3$ / 1.1 equiv of $PhMe_2SiH$ (as relative reaction times to consume starting $FpCOCH_3$):

$[(CO)_4Mn\text{-}Br]_2$ (10m) >> $(CO)_5Mn\text{-}Br$ (45m) >> $(CO)_5Mn\text{-}COPh$ (3h) >

$(CO)_5Mn\text{-}CH_3$ (4h) > $(CO)_5Mn\text{-}Ph$ (6h) > $(CO)_5Mn\text{-}CH_2Ph$ (9h) > $(PPh_3)(CO)_4Mn\text{-}COPh$ (12h) >

$(CO)_5Mn\text{-}COCH_3$ (12h) >> $(PPh_3)(CO)_4Mn\text{-}COCH_3$, $(CO)_5Mn\text{-}SiMe_2Ph$, $Mn_2(CO)_{10}$,

This ranking however varies somewhat with the choice of hydrosilane. With the dihydrosilanes, $CH_3Mn(CO)_4(PPh_3)$ and $CH_3C(O)Mn(CO)_4(PPh_3)$ now are the most reactive precatalysts (< 35 m), although such obvious candidates as $PhMe_2SiMn(CO)_5$, $Me_3SiMn(CO)_5$, $HMn(CO)_5$, and $Mn_2(CO)_{10}$ still are inactive. Moreover, these PPh_3-substituted Mn complexes selectively afford mono-Fp(siloxyethyl) products, whereas the remaining catalysts generate 0.8-1.2 mixtures of mono- and bis-Fp(siloxyethyl) compounds (eq. 10). Analytically pure samples of all four products were procured by size-exclusion chromatography.

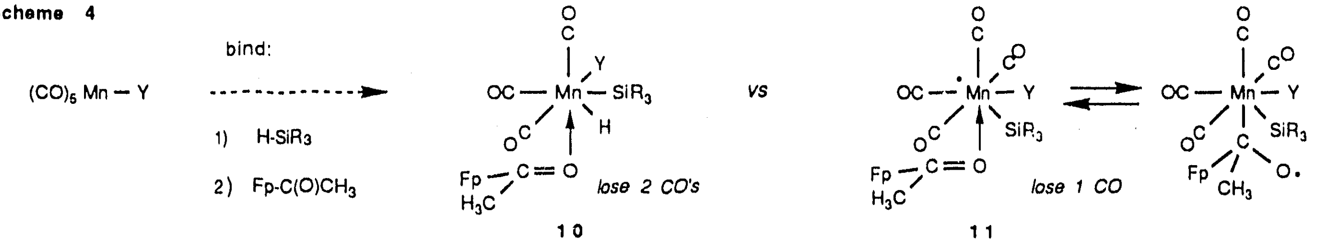


(1 0)

3. $YMn(CO)_5$-Catalyzed Hydrosilation of $Cp(CO)_2Fe$-$COCH_3$: Mechanistic Considerations

Work in progress emphasizes a study of the kinetics and mechanism of these surprisingly clean $FpC(O)CH_3$ hydrosilation reactions using $YMn(CO)_5$ complexes (Y = halide, alkyl, acyl) as precatalysts. These catalytic systems are homogeneous: catalytic activity of these clear yellow-to-orange solutions continues unabated in the presence of suspended mercury. We believe that the major issue concerns how the manganese center simultaneously binds $HSiR_3$ *and* $FpC(O)CH_3$, ie., whether it loses one or two carbonyls. Losing two carbonyls could give $(CO)_3(Y)Mn(H)(SiR'_3)[O{=}C(CH_3)Fp]$ (**10**, Scheme 4). This intermediate would be consistent with a "classical" catalysis mechanism that alternates 16-/18-electron intermediates, such as that postulated for $(PPh_3)_3RhCl$-catalyzed hydrosilation of ketones or $FpC(O)CH_3$.[31] We do not preclude this mechanism, but it appears unlikely that the manganese center would *catalytically* dissociate two carbonyls.

Scheme 4

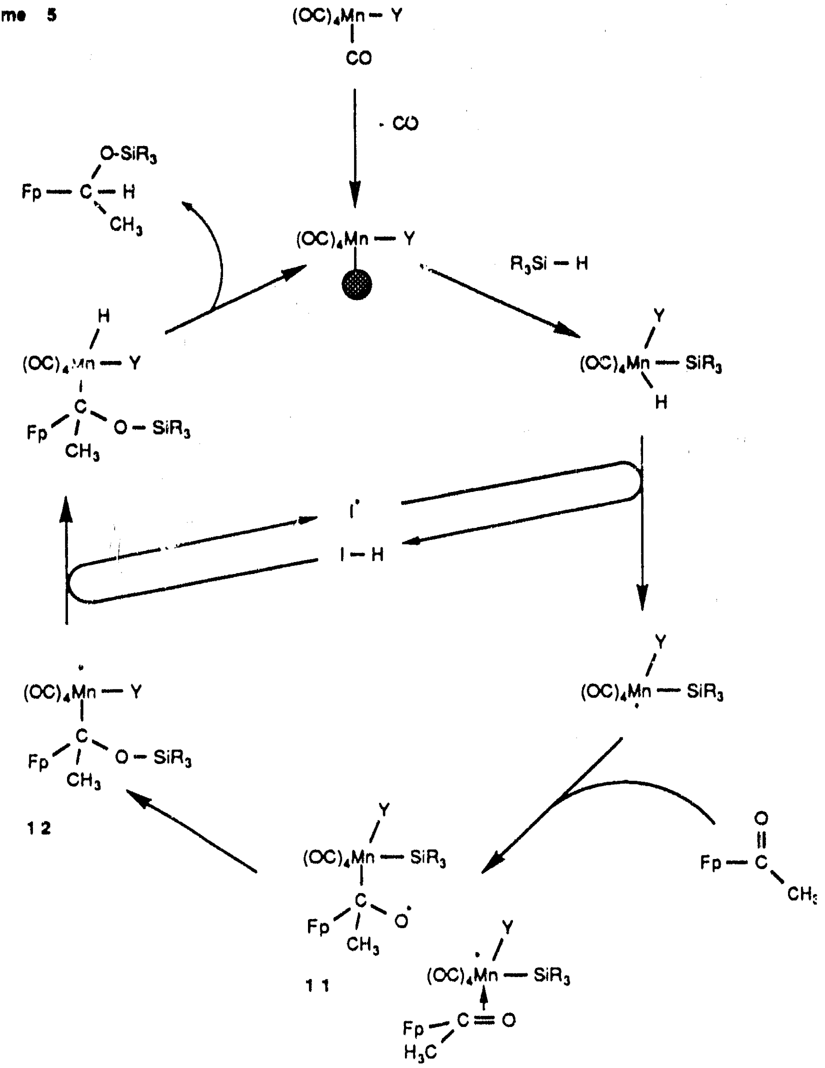


A more tenable mechanism entails the $YMn(CO)_5$ precatalyst dissociating only one carbonyl in ligating $HSiR_3$ and $FpC(O)CH_3$, thus engendering a free-radical mechanism. In this free-radical mechanism, a 17-electron species, resulting from hydrogen atom abstraction from the silane oxidative addition product $(CO)_4(Y)Mn(H)(SiR_3)$, then associates $FpC(O)CH_3$. The resulting 19-electron adduct[32] **11**, perhaps having its odd electron partially delocalized on the ligated $FpC(O)CH_3$, rearranges to a 17-electron manganese system Fp-$C(CH_3)(OSiR_3)$-$Mn(CO)_4(Y)\cdot$ (**12**) that shares a μ-siloxyalkylidene ligand with a Fp moiety. Subsequent hydrogen atom transfer and reductive elimination of $FpCH(OSiR_3)R$ as product then would regenerate the active catalyst, $YMn(CO)_4$.

This odd-electron sequence could function as a radical-chain mechanism. One possibility appears in Scheme 5, and is based on Brown's radical-chain mechanism for CO substitution by phosphine on metal hydride complexes, eg., $HMo(CO)_3Cp$ or $HMn(CO)_5$.[33] According to this scheme, the hydrogen atom abstractor $I\cdot$ could be an adventitious radical or even the 17-electron species $(CO)_4(Y)Mn(SiR_3)\cdot$. A supporting observation for this free-radical mechanism is that trityl radical, $Ph_3C\cdot$, blocks the $YMn(CO)_5$-catalyzed hydrosilation of $FpC(O)CH_3$, vide infra.

Proposed studies are concerned with characterizing the independently generated silane oxidative addition intermediate $(CO)_4(Y)Mn(H)(SiR_3)$. Several examples of related (hydrido)(silyl)(alkyl)Co(III),[34a,b] (hydrido)(silyl)$_2$Co(III),[34c] and (hydrido)(silyl)$_2$Fe(CO)Cp[34d] species are known. Alternatively, hydrosilane ligated (η^2-H-Si) on manganese could function as the reactive intermediate.[35]

Scheme 5

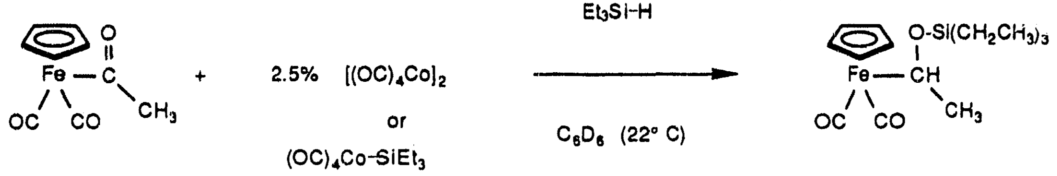


4. $Cr_2(CO)_8$ -Catalyzed Hydrosilation of $Cp(CO)_2Fe$-$COCH_3$

We established that $Co_2(CO)_8$ functions as a moderately active hydrosilation catalyst towards $FpC(O)CH_3$. Although not as reactive as manganese acyls, $Co_2(CO)_8$ catalyzes the addition of Et_3SiH across $FpC(O)CH_3$, for example, and affords $FpCH(OSiEt_3)CH_3$ in moderate yield. Important observations are that (1) these reactions proceed by an initial burst of high reactivity, and (2) the cobalt silyl complex $(CO)_4Co$-$SiEt_3$[36] is much less active as a catalyst (cf. Table 2). These reactions can be run to completion, starting with 1:1 $FpC(O)CH_3$ and Et_3SiH, by slowly adding the same $Co_2(CO)_8$ catalyst solution to the reaction mixture.

These observations preclude $(CO)_4Co$-$SiEt_3$ as the major precatalyst. This is surprising because $Co_2(CO)_8$ readily cleaves with Et_3SiH under the reaction conditions and gives $(CO)_4Co$-$SiEt_3$,[36g] a reaction of presumed importance to $Co_2(CO)_8$-catalyzed reactions of hydrosilanes with aldehydes and CO[23,24] and with alkenes.[34a,37] A plausible explanation for our results is that Et_3SiH adds to the intact dimer, eg., as $(CO)_4Co$-$Co(H)(SiEt_3)(CO)_3$, and this adduct not $(CO)_4Co$-$SiEt_3$ provides the active catalyst. Similar "oxidative addition" of H-SiR3 to an intact metal carbonyl dimer has been reported by Brown for $Mn_2(CO)_{10}$ under photochemical conditions.[38] Further studies are in progress on using $Co_2(CO)_8$ and related dimers $Co_2(CO)_{8-x}(L)_x$ ($L = PR_3$ and $L_2 = \eta^4$-diene; x = 2 or 4) as $FpC(O)CH_3$ hydrosilation catalysts under thermal conditions (i.e., room temperature).

Table 2 **$Co_2(CO)_8$-Catalyzed Hydrosilation of $FpC(O)CH_3$**



Time (hrs)	% Product Formed using {Catalyst} { [(OC)₄Co]₂ }	 { (OC)₄Co-SiEt₃ }
0.25	24	5
1.5	31	11
3.5	37	16
15	43	30
50	56	17*

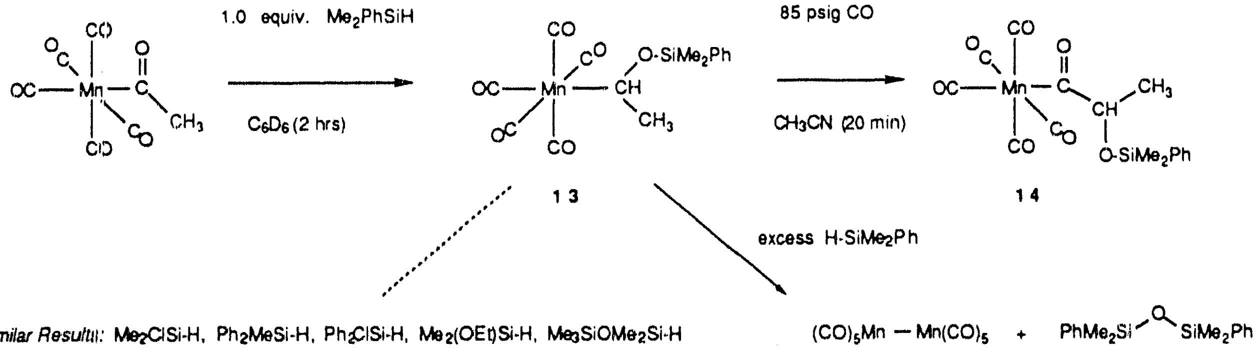
B. Homogeneous Hydrosilation of Manganese and Cobalt Acyl Complexes

1. Hydrosilation of Manganese Acyl Complexes $RC(O)Mn(CO)_5$.

The addition of mono- and dihydrosilanes across the acyl ligand of labile manganese complexes $RC(O)Mn(CO)_5$ (R = CH_3, Ph), as opposed to reductively cleaving the acyl, represents a new organometallic reaction. Me_2PhSiH, for example, quantitatively transforms $CH_3C(O)Mn(CO)_5$ to its fully characterized α-siloxyethyl compound **13**, which was carbonylated to give its acyl derivative **14** (85% isolated yield after chromatography) (Scheme 6). Analogs of **13** and **14** with R_3Si = $SiPh_2Me$, $Si(OEt)Me_2$, and $SiMe_2OSiMe_3$ are in the final stages of their full characterization.

The resulting stable α-siloxyethyl compounds are very reactive towards free hydrosilane. Treatment of $CH_3CH(OSiMe_2Ph)Mn(CO)_5$ (**13**) (or even $CH_3Mn(CO)_5$) with additional $HSiMe_2Ph$ in benzene at room temperature slowly liberates mixtures of the disiloxane $(Me_2PhSi)_2O$, $Mn_2(CO)_{10}$, and unidentified organic materials. The independently characterized manganese silyl $Me_2PhSiMn(CO)_5$ does not initially form. Difficulties in isolating other manganese α-siloxyethyl compounds $CH_3CH(OSiR_3)Mn(CO)_5$ are in part due to similar reactions with free hydrosilane.

Scheme 6 Monohydrosilanes and their reactions with $(CO)_5Mn\text{-}COCH_3$



Similar Results: $Me_2ClSi\text{-}H$, $Ph_2MeSi\text{-}H$, $Ph_2ClSi\text{-}H$, $Me_2(OEt)Si\text{-}H$, $Me_3SiOMe_2Si\text{-}H$

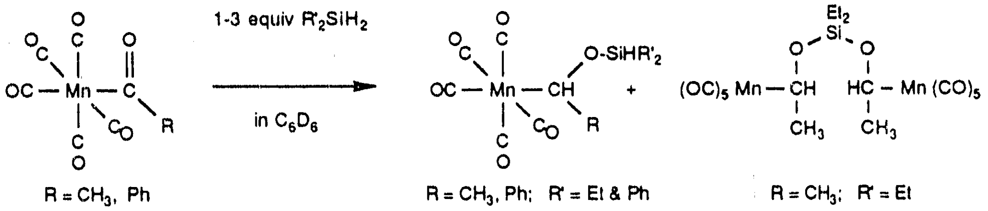
Competing Reaction: $(CO)_5Mn\text{-}CH(OSiR_3)CH_3$ *plus* $(CO)_5Mn\text{-}C(OSiR_3)\text{=}CH_2$

R_3Si = Et_3Si, Et_2MeSi, $EtMe_2Si$

No Reaction: $(MeO)_3Si\text{-}H$, $(EtO)_2MeSi\text{-}H$. *Ph_3SiH:* $(CO)_5Mn\text{-}CH_2CH_3$

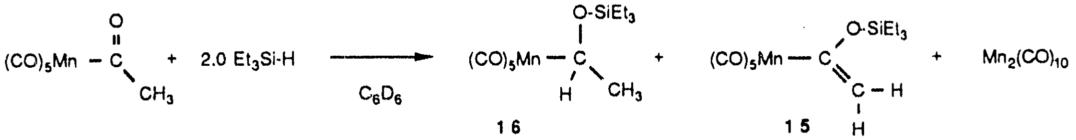
- These manganese acyl hydrosilation reactions (1) occur rapidly and quantitatively at room temperature using 1-2 equiv. of hydrosilane, (2) are inhibited by the presence of CO (1 atm), (3) do not afford free aldehyde, and (4) do not require a catalyst.[19] The starting manganese acetyl and benzoyl complexes (R = CH_3, Ph), however, function as excellent hydrosilation catalysts for aldehydes and other organotransition metal acyl compounds.[16,19,21]

Dihydrosilanes Ph_2SiH_2 or Et_2SiH_2 also rapidly consume manganese acyl compounds and quantitatively produce α-siloxyalkyl compounds (eq. 11). These reactions differ, however, in that excess dihydrosilane (typically 2-3 fold) must be used, although the products slowly decomposed.



(1 1)

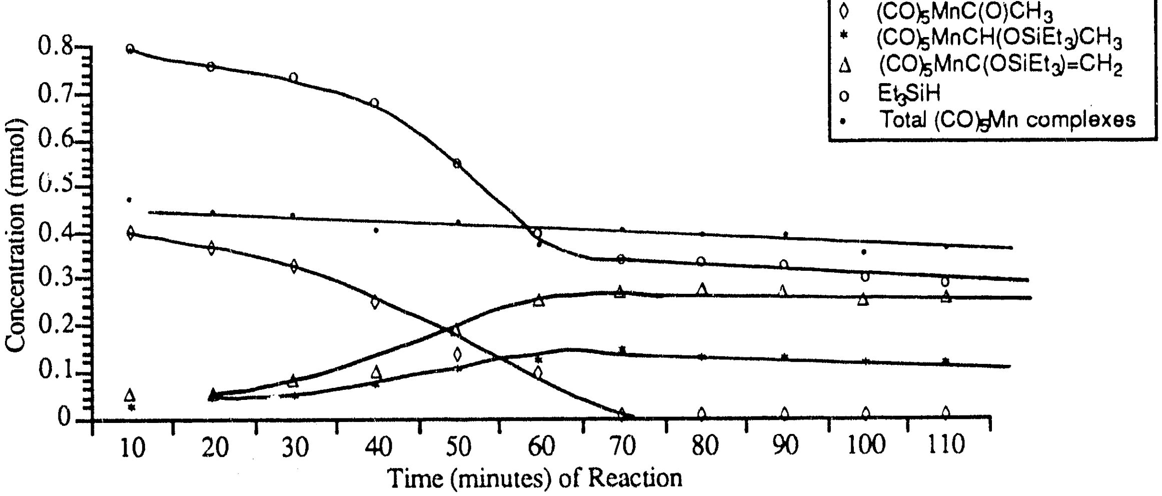
Triethylsilane is unusually reactive towards manganese acetyl $CH_3C(O)Mn(CO)_5$, since it generates 2:1 mixtures containing $CH_2{=}C(OSiEt_3)Mn(CO)_5$ (**15**) as well as $CH_3CH(OSiEt_3)Mn(CO)_5$ (**16**) (eq. 12).[39] These products form independently, as established by a reaction profile study (Figure 1): **16** does not transform to **15**. Multinuclear NMR spectral monitoring (^1H, ^{13}C, ^{29}Si) of reaction mixtures containing $CH_3C(O)Mn(CO)_5$ and 1.2-2.0 equiv of $HSiEt_3$ further revealed that $CH_3CH(OSiEt_3)Mn(CO)_5$ (**16**) plus additional $HSiEt_3$ degrades to $Mn_2(CO)_{10}$ and $(Et_3Si)_2O$, but not to $Et_3SiMn(CO)_5$. We detected neither acetaldehyde nor its hydrosilation product, $CH_3CH_2OSiEt_3$.



(1 2)

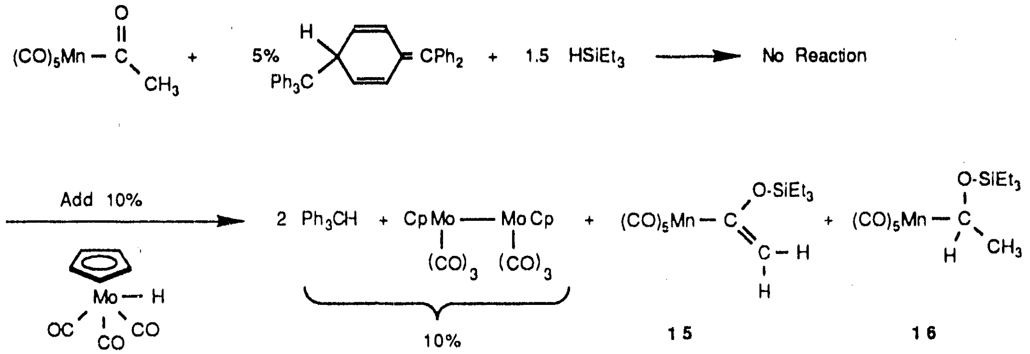
In initial mechanistic studies, we attempted to selectively inhibit the triethylsilane hydrosilation of $CH_3C(O)Mn(CO)_5$ in order to preferentially give either **15** or **16**. For example, adding carbon monoxide (1 atm) inhibits this hydrosilation; switching to THF as the solvent doubles the reaction time and gives only **15**; using $HSiMe_2Ph$ / $HSiEt_3$ mixtures selectively forms $CH_3CH(OSiMe_2Ph)Mn(CO)_5$ (**13**) plus **16**, but much less **15**.

Figure 1 Reaction Profile. $CH_3C(O)Mn(CO)_5$ plus 1.84 equiv. of $HSiEt_3$. Concentrations via ^1H NMR



Dramatic results on perturbing the manganese acetyl hydrosilation were observed by adding small amounts of the trityl dimer, alone and in combination with $HMo(CO)_3Cp$ (Scheme 7). Only 5% $(Ph_3C)_2$, which reversibly dissociates trityl radical ($Ph_3C\cdot$), with respect to $CH_3C(O)Mn(CO)_5$ blocked its conversion to **15** and **16** for at least 1.5 h. Adding 10% $HMo(CO)_3Cp$ during this time immediately initiates the hydrosilation; and after another 80-100 minutes, all $CH_3C(O)Mn(CO)_5$ had converted to the usual 2:1 mixture of **15** and **16**. Presumably, the $Ph_3C\cdot$ scavenges a radical initiator or it otherwise blocks the hydrosilation reaction, prior to being deactivated by a metal hydride hydrogen atom donor.[40]

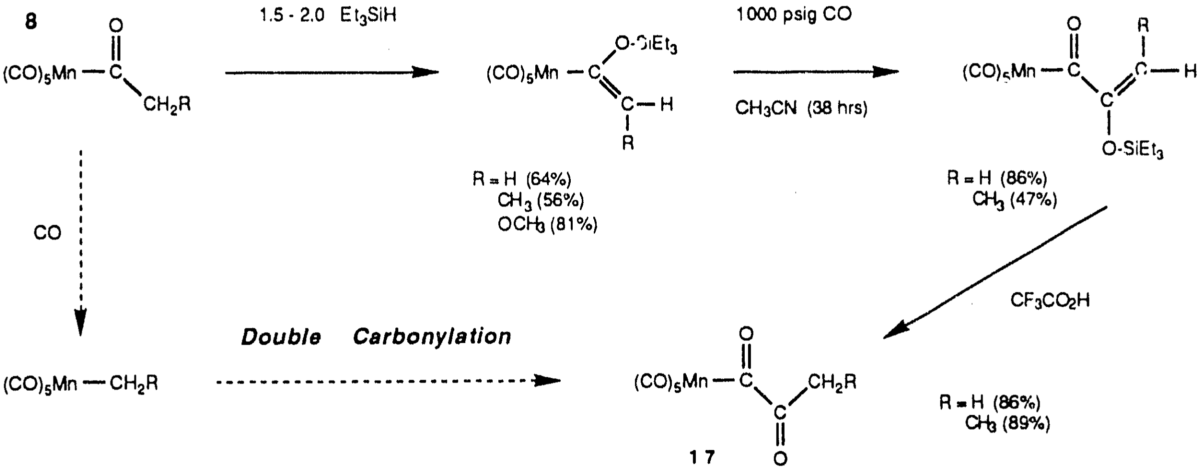
Scheme 7



Hydrosilation of the manganese propionyl and methoxyacetyl complexes $RCH_2C(O)Mn(CO)_5$ ($R = CH_3, OCH_3$) with triethylsilane in benzene affords stable α-triethylsiloxyvinyl products (Z)-$RCH{=}C(OSiEt_3)Mn(CO)_5$ (Scheme 8) in moderate yields (56-77%).[39] Z-configurations were assigned on the basis of NOE difference spectroscopy. Carbonylation of two α-siloxyvinyl complexes (R = H, Me) afforded the siloxyvinylacyl compounds depicted; protonation gave the α-ketoacyl derivatives $RCH_2C(O)C(O)Mn(CO)_5$ (**17**) ($R = H, CH_3$).

The overall set of ligand reactions involved in transforming manganese methyl and ethyl complexes $RCH_2Mn(CO)_5$ into their α-ketoacyl derivatives $RCH_2C(O)C(O)Mn(CO)_5$ (**17**, $R = H, CH_3$) represents a novel form of double carbonylation.[41] The hydrosilation step and carbonylation of the resulting (α-triethylsiloxy)vinyl derivatives $RCH{=}C(OSiEt_3)Mn(CO)_5$ supplants the disfavored carbonylation of the acyl complexes $RCH_2C(O)Mn(CO)_5$.[42]

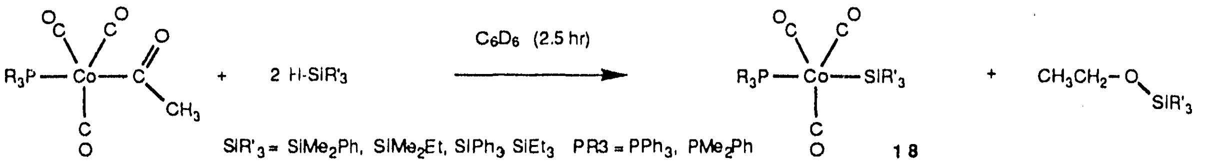
Scheme 8



The reactivity of $PhC(O)Mn(CO)_5$ towards $HSiEt_3$ and $HSiMe_2Ph$ differed in that benzyl silylethers formed (Scheme 3, $L_xM = Mn(CO)_5$). A plausible pathway for this reaction requires hydrosilation-then-reductive elimination of the coordinatively unsaturated intermediate $PhCH(OSiR'_3)Mn(CO)_4$. This pathway resembles the one that we proposed for the hydrosilation of $CH_3C(O)Co(CO)_3(PPh_3)$ to directly give $CH_3CH_2OSiR'_3$ (i.e., Scheme 9).[20]

2. Hydrosilation of Cobalt Acetyl Complexes $CH_3C(O)Co(CO)_3(PR_3)$

Cobalt acetyl compounds $CH_3C(O)Co(CO)_3(PR_3)$ differ from their manganese analogs in their reactions with monohydrosilanes. Stoichiometric hydrosilation occurred exclusively at the cobalt center to give equimolar amounts of cobalt silyl compounds **18** and ethoxysilanes, irrespective of using 1 or 2 equiv. of hydrosilane (eq. 13). Neither acetaldehyde nor α-siloxyethyl products $CH_3CH(OSiR'_3)Co(CO)_3(PR_3)$ were detected. The presence of either CO (1 atm) or one equiv. of free phosphine inhibits these reactions, but adding catalytic quantities of Wilkinson's compound, $RhCl(PPh_3)_3$, affects neither the rate nor the outcome. (Previously undocumented phosphine lability on $CH_3C(O)Co(CO)_3(PR_3)$ is evident by up to 20% exchange over 2 h of PPh_2(p-tolyl) for ligated PPh_2Me during these inhibition studies.)



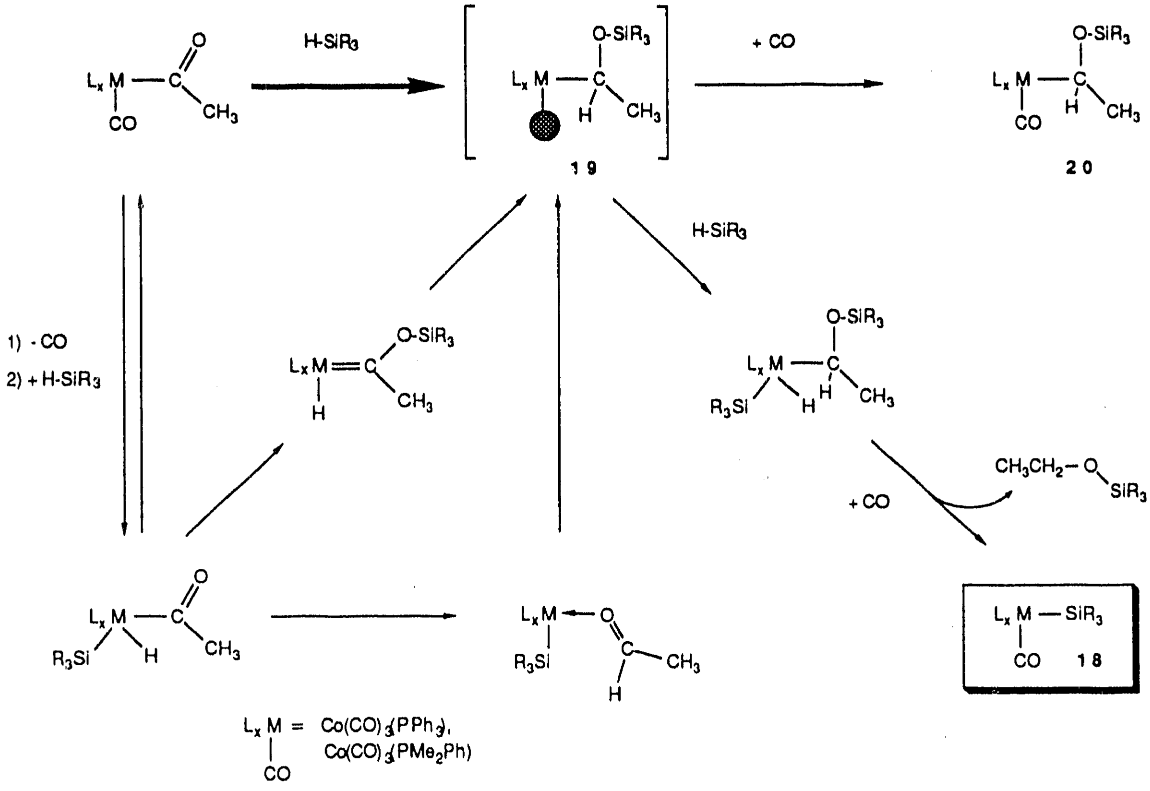
(13)

Acetaldehyde and benzaldehyde interrupt the reaction of $CH_3C(O)Co(CO)_3(PMe_2Ph)$ with $HSiMe_2Ph$, albeit by very different pathways. Acetaldehyde selectively undergoes hydrosilation (under stoichiometric or catalytic conditions) to give $CH_3CH_3OSiMe_2Ph$, while leaving the cobalt acetyl intact. Benzaldehyde under similar conditions effectively sequesters the cobalt acetyl and blocks all hydrosilation activity, including aldehyde hydrosilation. (In contrast, hydrosilation of PhCHO with $HSiMe_2Ph$ and catalytic $CH_3C(O)Mn(CO)_5$ is quite facile under these conditions.[16]) Even including an equivalent amount of acetaldehyde failed to induce any hydrosilation reaction; the benzaldehyde now blocked hydrosilation of the acetaldehyde. This blocking of catalytic hydrosilation activity with a competing but less reactive substrate previously has been observed: for example, the presence of inert FpC(O)Ph prevents hydrosilation of $CH_3C(O)Mn(CO)_5$.

We also characterized and examined the reactivity of several cobalt silyl complexes[43] $R'_3SiCo(CO)_3(PR_3)$ (**18**). Surprisingly, $Me_2PhSiCo(CO)_3(PMe_2Ph)$ (**18a**) neither interacts with excess CH_3CHO in C_6D_6, nor does it catalyze aldehyde hydrosilation[31] under conditions that $CH_3C(O)Co(CO)_3(PPh_2Me)$ functions as an efficient catalyst. The absence of silane exchange,[44] involving **18a** and $HSiEt_3$ under thermal conditions, likewise indicates the absence of CO or phosphine ligand lability. In contrast, the more reactive (labile) cobalt tetracarbonyl silyl complexes $R''_3SiCo(CO)_4$ (R'' = Me, Et) easily add *iso*-butyraldehyde[24b] to apparently provide (undetected) α-siloxyalkyl intermediates $Me_2CHCH(OSiR''_3)Co(CO)_4$[24] and undergo facile silane exchange at room temperature.

The inertness of $PhMe_2SiCo(CO)_3(PPh_2Me)$ towards acetaldehyde, even in the presence of excess $HSiMe_2Ph$, clearly limits the mechanistic options that are available for transforming cobalt acetyl compounds $CH_3C(O)Co(CO)_3$ (PMe_2Ph) into their silyl derivatives **18** plus ethoxysilane. We favor an intramolecular pathway (summarized in Scheme 9) that resembles those advanced by Murai et.al. for $Co_2(CO)_8$-catalyzed siloxymethylation of aldehydes (with $HSiR_3$ and CO) to higher α-siloxy aldehydes[23,24,45] and by Akita, Moro-aka, et.al. for their reduction of the acyl ligand on $Cp(L)(CO)FeC(O)CH_2CH_2Ph$ complexes via catalytic hydrosilation.[25] In our version of this pathway, a coordinatively unsaturated α-siloxyethyl intermediate **19** can give either an α-siloxyethyl product **20** (eg., $M(CO)L_x = Mn(CO)_5$) or a silyl complex **18**, $M(CO)L_x = Co(CO)_3(PR_3)$.

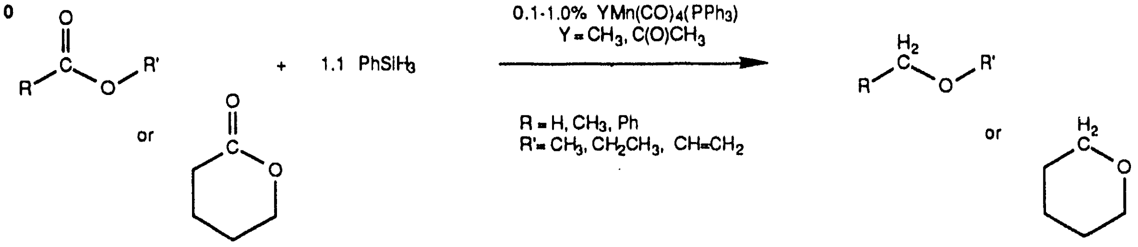
Scheme 9 **Proposed Pathways for Hydrosilation of Labile Organometallic Acyl Complexes**



C. Homogeneous Hydrosilation of Organic Esters

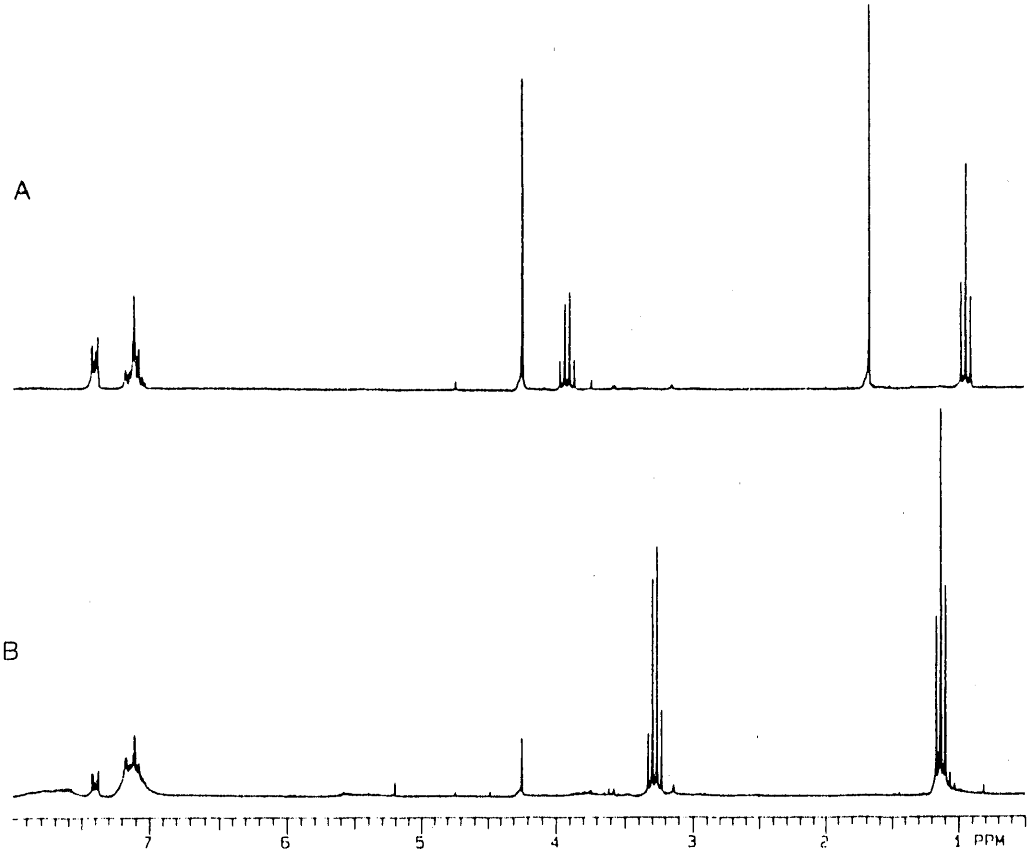
We have recently established that several manganese complexes catalytically reduce organic esters with hydrosilanes (Scheme 10). Thus $PhSiH_3$ and ≤ 2% $CH_3C(O)Mn(CO)_4(PPh_3)$ *quantitatively* reduce a number of esters to their ethers. These exothermic reactions are complete in < 45 min, with no other organic products detected by ^1H and ^{13}C NMR spectroscopy. A typical set of ^1H NMR spectra for the $PhSiH_3$ reduction of ethyl acetate are enclosed, Figure 2. Interestingly, $CH_3Mn(CO)_5$ is nearly as reactive as a catalyst, but $BrMn(CO)_5$ is much less active. Work remaining to be done on this ester reduction reaction includes quantifying (LC/GLC procedures) and isolating the organic ethers, further extending the synthetic scope (amides/lactams?), varying the silane and manganese catalyst, and of course probing the mechanism. Substituting H_2SiPh_2 for $PhSiH_3$ affords the same high reactivity, but siloxyacetal products $RCH(OSiHPh_2)(OR')$ appear as the only organic products.

Scheme 10



Very little precedent exists for directly reducing esters to ethers![46] Our ester hydrosilation reaction differs considerably from that recently reported by Buchwald's group.[47] They demonstrated that titanocene, Cp_2Ti, catalytically reduces esters $RC(O)OR'$ with $HSi(OEt)_3$ to silyl ethers $RCH_2OSi(OEt)_3$, apparently via an intermediate aldehyde

Figure 2

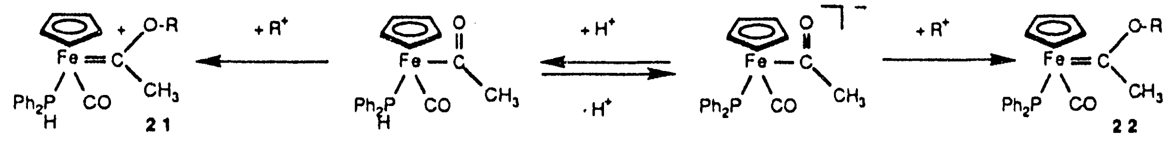


^{1}H NMR spectrum (200 MHz) of the reaction: $CH_3CO_2CH_2CH_3$ (23 mg, 0.261 mmol), $PhSiH_3$ (28 mg, 0.261 mmol), and $(CO)_5MnCH_3$ (1 mg, 5×10^{-3} mmol 1.8%) in 600 mg C_6D_6. Spectral scan A: t=0; scan B: t = 45 min.

hydrosilation step. Our ester hydrosilation represents a major breakthrough for my DOE-sponsored research program for two reasons: (1) We have an extremely efficient homogeneous catalytic procedure for carrying out an otherwise difficult organic reduction, and (2) this hydrosilation procedure should prove to be mechanistically challenging.

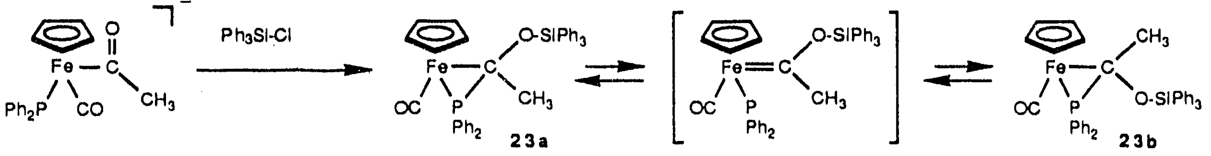
IV. Phosphide Iron Acyl Chemistry

The presence of a phosphine-phosphide[48] "molecular switch", reversibly interconverting ligated diphenylphosphine and diphenylphosphide ligands,[49] on $Cp(PPh_2H)(CO)FeR$ / $Cp(PPh_2)(CO)FeR^{-1}$ complexes potentially could regulate the reactivity of the alkyl and acyl ligands. Using this switch on iron acetyl complexes (eq. 14), we could in principle selectively generate cationic[50] or neutral[51] carbenoid species (**21** and **22**, respectively), each could engender opposite diastereoselectivity as hydride acceptors.[30,52] Alkylating the (phosphido)iron acetyl, however, is not straightforward. Both MeI or MeOTf alkylate the phosphide center (giving $Cp(PPh_2Me)(CO)Fe\text{-}COCH_3$) instead of generating the methoxycarbene complex.[53]



(14)

We documented the above phosphine/phosphide reaction chemistry and found that the (phosphido)iron methyl compounds do not carbonylate (85 psig CO in THF, with or without 10% $Cp_2Fe^+PF_6^-$ present) to give their acetyl derivatives. Under comparable conditions, the neutral methyl complexes $Cp(PPh_2Me)(CO)FeCH_3$ and $In(PPh_2H)(CO)FeCH_3$, for example, gave their acetyl compounds.



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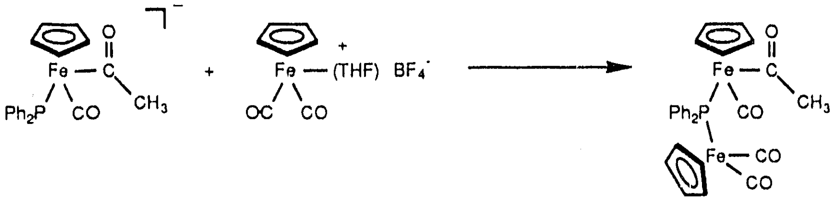
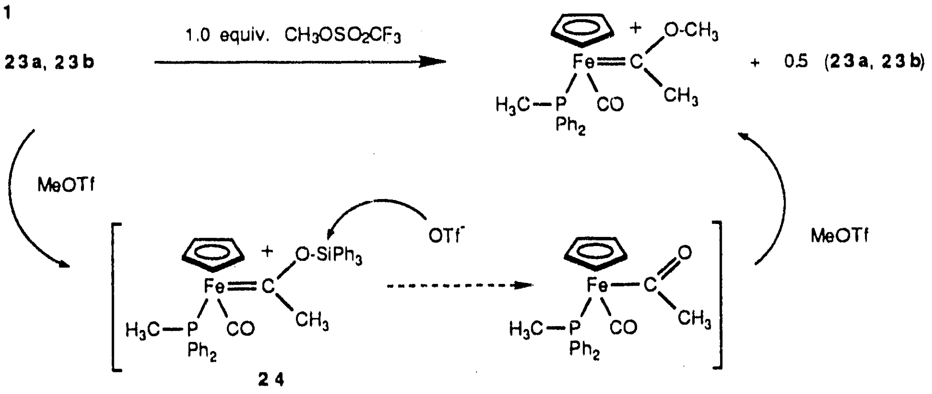
Silyl chlorides, R_3SiCl (R_3 = Me_3Si, Me_2t-BuSi, and Ph_3Si), silylate the acyl oxygen center, but they afford manganese α-siloxyethyl metallacyclic complexes.[54] With Ph_3SiCl, this metallacycle exists as a 30:70 mixture of two diastereomers **23a**, **23b**; these slowly equilibrate in solution with a rate constant, k = 0.074 sec^{-1} (^1H NMR magnetization transfer study). An X-ray structure determination of the less soluble syn (O-O) diastereomer **23b** was performed. An attractive pathway for interconverting these metallacyclic diastereomers entails transience of a siloxycarbene intermediate, which rotates about the iron-carbon (carbene) bond. Although we did not detect the isomeric siloxycarbene intermediate, it has been intercepted and derivatized.

Initial attempts to intercept the postulated siloxycarbene complex by protonating diastereomeric mixtures of **23a**, **23b** with CF_3SO_3H or HBF_4 proved to be uninformative, as were the reactions with $FpTHF^+ BF_4^-$. This latter result proved disappointing, since we successfully have used Fp^+ Lewis acids to metalate the phosphide ligand on $Cp(PPh_2)(CO)FeC(O)CH_3^{-1}$.[55] Studies in progress are concerned with further characterizing the resulting $Cp(CO)_2Fe$-PPh_2-$Fe(CO)Cp(COCH_3)$ by electrochemical procedures, as part of our exploratory work on oligomeric μ-phosphide compounds.[56]



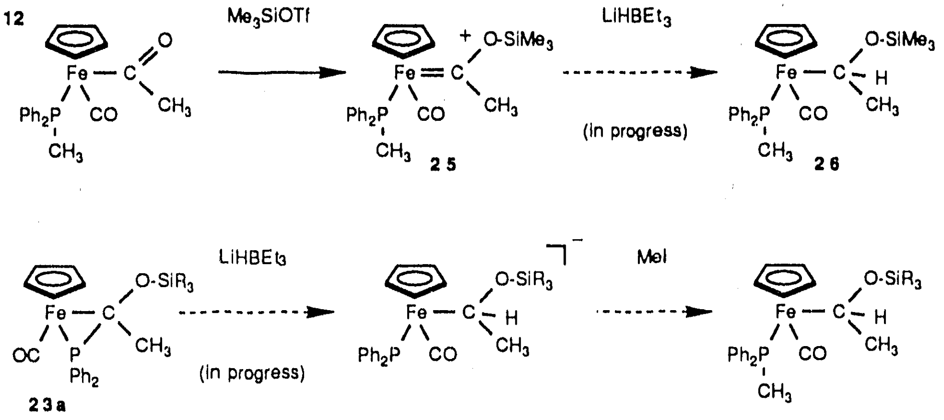
The electrophilic alkylating agent methyl triflate derivatizes **23a**, **23b** presumably by trapping the siloxycarbene intermediate (Scheme 11). Two equivalents of methyl triflate are required in order to smoothly form the methoxycarbene compound $Cp(PPh_2Me)(CO)Fe{=}C(OMe)CH_3^+ OTf^-$. The postulated reaction pathway is illustrated. Key steps entail desilylating the hypothesized siloxycarbene intermediate **24** by the triflate counterion and then alkylating the resulting acetyl compound with the second equivalent of MeOTf.

Scheme 11



We have synthesized the trimethylsiloxycarbene compound **25** (Scheme 12) in order to address the reaction chemistry of the hypothesized triphenylsiloxycarbene **24**. Trimethylsilyltriflate (one equiv.) quantitatively silylates the acetyl compound Cp(PPh$_2$Me)(CO)FeCOCH$_3$ and produces **25**, which although extremely moisture sensitive is stable in CH$_2$Cl$_2$ solution. We anticipate no difficulty in fully characterizing this molecule, but we now must account for its stability vs the postulated instability (with respect to triflate counterion) of **24**. We are very interested in examining the reactivity of **25** with nucleophilic hydride donors, as illustrated. The anticipated siloxyethyl product **26** obviously relates to our ongoing hydrosilation studies, especially if we get **26** with high diastereoselectivity. In related studies, we also are studying the reactions of borohydride reagents with **23a**, **23b**.

Scheme 12



TIME AND EFFORT COMMITMENT TO PROJECT

The principal investigator has devoted approximetely 40% of his time during the academic year and 100% during two summer months on this project. It is anticipated that about the same time and effort commitment will be maintained during the remainder of the current term.

PUBLICATIONS

Appearing During Granting Period and Acknowledging DOE Support

1. "Preparation of Some Bimetallic μ-(η^1-C,O) Acetyl Complexes", T. C. Forschner and A. R. Cutler, *Inorganic Synthesis* **1989**, ***26***, 231.

2. "Interconversion of Acetyl-and Terminal- Carbonyl Groups on Labeled (η^5-Indenyl) $(CO)_2$ Fe-$^{13}C(O)CH_3$", T. C. Forschner and A. R. Cutler, *J. Organomet. Chem.* **1989**, ***361***, C41.

3. "Carbonylation of (η^5-Indenyl)$(CO)_2$Fe-α-Alkoxyalkyl Complexes Using Bimetallic α-Alkoxyacyl Intermediates", S. A. Levitre, A. R. Cutler, and T. C. Forschner, *Organometallics* **1989**, ***8***, 1133.

4. "$RhCl(PPh_3)_3$-Catalyzed Hydrosilation of Organoiron Acyl Complexes", E. J. Crawford, P. K. Hanna, and A. R. Cutler, *J. Am. Chem. Soc.* **1989**, ***111***, 6891.

5. "Manganese Carbonyl Complexes as Hydrosilation Catalysts towards Organoiron Acyl Compounds", P. K. Hanna, B. T. Gregg, and A. R. Cutler, *Organometallics* **1991**, ***10***, 31.

6. "Hydrosilation of Manganese Acyls $(CO)_5MnCOR$ ($R = CH_3$, Ph)", B. T. Gregg, P. K. Hanna, E. J. Crawford,, and A. R. Cutler, *J. Am. Chem. Soc.* **1991**, ***113***, 384.

7. "Catalyzed and Noncatalyzed Hydrosilation of Organotransition Metal Acyl Complexes", P. K. Hanna, B. T. Gregg, D. L. Tarazano J. R. Pinkes, and A. R. Cutler, *Advances in Chemistry : New Science in Homogeneous Transition Metal Catalyzed Reactions* **1992** in press.

8. "Synthesis and Solution Dynamics of $[Cp(CO)_2Fe]_2(CH{=}CH_2)^+PF_6^-$, a μ-(η^1:η^2) Vinyl Complex Not Containing a Metal-Metal Bond", L. Tarazano, T.W. Bodnar, T.C. Forschner, and A. R. Cutler, *J. Organomet. Chem.* **1992**, in press.

9. "Reactivity of Cobalt Acetyl Complexes $(PR_3)(CO)_3CoCOCH_3$ with Monohydrosilanes", B. T. Gregg and A. R. Cutler, *Organometallics* **1992**, in press.

10 "Electrophilic Activation, Reduction, and Carbonylation of the Acetyl Ligand On $(PPh_3)(CO)_3CoCOCH_3$", C. C. Tso and A. R. Cutler, *Polyhedron* **1992**, in press.

11. "(η^5-C_5H_5)(CO)Fe$(CH_3CN)_2^+$ as a Synthetic Intermediate in Preparing Disubstituted Compounds (η^5-C_5H_5)(CO)Fe$(L_1)(L_2)$", A. B. Todaro, L. D. Tarazano, A. R. Cutler, and J. J. Benoit, manuscript submitted.

12. "Transformation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ ($R = H, CH_3, OCH_3$) into their Siloxyvinyl Derivatives $(CO)_5MnC(OSiEt_3){=}CHR$ with Triethylsilane, An Approach to Double Carbonylation of Manganese Alkyl Complexes $(CO)_5MnCH_2R$", B. T. Gregg and A. R. Cutler, manuscript submitted.

Manuscripts in Preparation

13. "Diastereofacial Selective Reduction of Phosphite-Substituted Alkoxycarbene Complexes $(\eta^5\text{-}C_5H_5)(P(OR)_3)(CO)Fe{=}C(OCH_3)CH_3{}^+PF_6{}^-$", P. K. Hanna, G. A. O'Doherty, E. J. Crawford, and A. R. Cutler.

14. "Unusual Carbonylation Reactivity of (η^5-Indenyl)ruthenium Methyl Complexes $(\eta^5\text{-}C_9H_7)(L_1)(L_2)RuCH_3$ (L_1, L_2 = CO, PPh_3, $Ph_2PCH_2CH_2PPh_2$)", R. J. Chiulli, D. L. Tarazano, and A. R. Cutler.

15. "Carbonylation of Alkoxymethyl and α-Alkoxyethyl Complexes $(\eta^5\text{-}C_9H_7)(CO)(PR_3)RuCHR(OMe)$ (PR_3 = CO, PPh_3, PEt_3, $P(OMe)_3$) Affords Different Products, $(\eta^5\text{-}C_9H_7)(CO)(PR_3)RuC(O)CH_2(OMe)$ and $(C_9H_7)(CO)(PR_3)RuC(O)CH_2CH_2OMe$", D. L. Tarazano, R. J. Chiulli, and A. R. Cutler.

16. "Hydrosilation of Manganese Acyl Complexes $(CO)_5MnCOCH_2R$ (R = H, CH_3, OCH_3) with monohydrosilanes", B. T. Gregg, E. J. Crawford, and A. R. Cutler.

17. "Rhodium-Catalyzed Hydrosilation of Ruthenium Acetyl Complexes $Cp(L)(CO)RuCOCH_3$ and $(\eta^5\text{-}C_9H_7)(L)(CO)RuCOCH_3$ (L = CO, PPh_3, PEt_3) and their Conversion to Vinyl Derivatives", D. L. Tarazano and A. R. Cutler.

18. "Diastereoselective Hydrosilation of Iron Acetyl Complexes $Cp(L)(CO)FeCOCH_3$ (L = PPh_3, PEt_3, $P(OMe)_3$, $P(OPh)_3$) using Rhodium Catalysis", J. R. Pinkes and A. R. Cutler.

19. "Organoiron Phosphido-Acetyl and -Methyl Complexes $(\eta^5\text{-}C_5H_5)(CO)(PPh_2)Fe\text{-}X^-$ and $(\eta^5\text{-}C_9H_7)(CO)(PPh_2)Fe\text{-}X^-$ (X = $COCH_3$ and CH_3), their Interconversion, and Reactions with Electrophiles", A. B. Todaro and A. R. Cutler.

20. "Bridging Phosphide Complexes Derived from $Cp(CO)_2Fe\text{-}PPh_2\text{-}Fe(CO)_2Cp^+$ and their Reactions with $Cp(CO)_2Fe\text{-}PPh_2$", M. E. Giuseppetti-Dery, A. R. Cutler, and T. C. Forschner.

21. "Reactivity of an Iron Phosphide Acetyl Complex $Cp(PPh_2)(CO)FeCOCH_3{}^-$ with Silyl Chlorides", Z. Mao, A. B. Todaro, and A. R. Cutler.

22. "Conversion of an Iron Phosphide Acetyl Complex $Cp(PPh_2)(CO)FeCOCH_3{}^-$ to a Bridging Phosphide Bis-Iron Acetyl Compound $Cp(CO)_2Fe\text{-}PPh_2\text{-}Fe(CO)(COCH_3)Cp$ and $(CO)_3Fe(\eta^4\text{-}C_5H_5PPh_2)Fe(CO)(COCH_3)Cp$", Z. Mao, A. B. Todaro, and A. R. Cutler.

12. "Synthesis and Reactions of the Organometallic Lewis Acids $(\eta^5\text{-}C_5H_5)_2WH^+SbF_6{}^-$ and $PF_6{}^-$", A. B. Todaro and A. R. Cutler.

13. "Bimetallic $\mu(\eta^1\text{-}C{:}\eta^1\text{-}O)$ Acetyl Complexes $Cp(L)(CO)Fe\text{-}C(CH_3)O\text{-}M^+$ {M= $Cp(CO)_2Fe$, $Cp(CO)_3Mo$, $Cp(CO)_3W$, and $Cp(NO)(CO)Re$} and {L = CO, PPh_3}, Their Characterization, Lability, and Reactions with Hydride Donors", A. B. Todaro, T. C. Forschner, C. C. Tso, and A. R. Cutler.

13. "Solution Dynamics of the Bimetallic Acetyl Complexes (η^5-Indenyl)(η^5-Cp) $(CO)_3Fe_2COCH_3{}^-$ Li^+, Na^+, and PPN^+ and their Reactions with Electrophiles", T. C. Forschner, B. T. Gregg, P. K. Hanna, and A. R. Cutler.

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